



# Adsorption of Ammonia on CaA (M-22) Zeolite Differential Heat and Mechanism

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**ABSTRACT:** The article presents the experimentally obtained values of the differential enthalpy of ammonia adsorption on LTA type CaA (M-22) zeolite at a temperature of 303 K. Enthalpy values were measured using an improved microcalorimeter of the Tianca-Calve type DAC-1-1A connected to a universal high-vacuum device. In zeolite CaA (M-22) of ammonia, a regular relationship between the amount of adsorption and differential enthalpy values, as well as the mechanism of adsorption from the initial area of adsorption to the area of reduction to the heat of condensation of ammonia and the regularity of filling the zeolite volume of ammonia molecules were determined. Under experimental conditions, the adsorption capacity of CaA (M-22) zeolite for ammonia was shown to be 10,5 mmol/g in 1 g of zeolite. From the regular change of the differential enthalpy values according to the amount of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  cations in the zeolite, initially in the first coordination sphere with the sodium cations in the zeolite sequentially until the tetramer  $4\text{NH}_3:\text{Na}^+$  ion-molecular complex, then the formation of the dimer  $2\text{NH}_3:\text{Ca}^{2+}$  ion-molecular complex with calcium cations, it was found that in the second coordination sphere, 2 more ammonia molecules interact with ammonia molecules adsorbed on calcium cations to form a general complex  $\text{Ca}^{2+}:2\text{NH}_3:2\text{NH}_3$ .

**KEYWORDS:** zeolite, silicalite, adsorption, enthalpy, volume, temperature, microcalorimeter, ammonia.

## I. INTRODUCTION

In order to obtain clean gas from primary natural gases, various environmental problems arise from year to year as a result of insufficient purification of additional chemicals contained in them, as well as the release of harmful gases from the burning of secondary gas in industry and production into the atmosphere. As a result of burning natural gas, the sulfur contained in it releases various sulfur compounds that are dangerous for humans, and a large amount of carbon (IV) oxide is released into the atmosphere, which has an increasing negative impact on human health. Therefore, the demand to prevent environmental problems is increasing year by year. Adsorbents are widely used to avoid these problems, that is, to dry and clean gases. In particular, the role of synthetic zeolites in the oil and gas industry is incomparable for their adsorption and catalytic properties. Therefore, it is important to synthesize zeolites with high adsorption and catalytic properties, to apply the results of research studies on increasing the level of their selectivity in practice.

Today, zeolites are widely used as adsorbents and catalysts in natural gas drying, oil and petroleum products processing industry. In order to increase the catalytic activity of zeolites and to scientifically substantiate them, it is necessary to regularly conduct fundamental research of the theoretical foundations of sorption processes in zeolites using scientific research methods that meet modern requirements. Nowadays, the widespread use of zeolites on an industrial scale and their use as catalysts is the cause of interest and research of many researchers [1].

It is known from the results of X-ray structural analysis that aluminosilicate zeolites of type A, X and Y are composed of cubic tetrahedral structural units. Each cubic tetrahedral  $\text{AlO}_4$  and  $\text{SiO}_4$  is composed of 24 structural unit tetrahedra, which are common to the tetrahedra with added oxygen ions. Therefore, each cuboctahedron is connected to 36 oxygen ions and 240 ions occupy (Al+Si) cuboctahedrons. Each cuboctahedron consists of six-four-membered and eight-six-membered windows [2].

Aluminum  $\text{AlO}_4$  oxide and  $\text{SiO}_4$  oxide zeolite tetrahedral lattice with "minus one" negative charge. Therefore, the tetrahedral zeolite framework requires the participation of an equivalent amount of cations. This requirement is related to the need to compensate for the excess electron charge in the  $\text{Al}_2\text{O}_4$  tetrahedral groups, in which Al has 3 independent s, p-electrons and forms electron pairs of equal value with each of the 4 oxygens surrounding it due to the attraction of one additional electron [3].



The difference in the aluminosilicate structure of A and X zeolites is the location of the cubic tetrahedral structural units in the phase, that is, in the voids [2; 4; 5;]. In type A zeolite, the cuboctahedrons form a regular cubic lattice. Each cuboctahedron is joined by six adjacent four-membered oxygen bonds. The spaces between the eight cuboctahedrons form large pores [3]. According to the Si/Al ratio of the zeolite, the amount of negative charges of the crystal lattice changes and different amounts of cations are introduced to fully or partially compensate. These cations can be alkali metals or alkaline earth metals. Adsorption and catalytic properties of zeolites change depending on the type of cation. Before using it in various fields of production industries, it is necessary to study its adsorption properties.

$\text{Ca}^{2+}$  and  $\text{Na}^+$  cations in type A CaA (M-22) zeolite are considered the main active centers, as well as the amount of cations is in different proportions, so the amount of adsorption of adsorbate molecules changes accordingly. By determining the main thermodynamic characteristics of the adsorption of test molecules such as polar water and ammonia, the amount, nature and strength of energetically active centers in the same type of crystallographic positions are determined [15-24].

The analysis of the literature showed that the main thermodynamic properties and adsorption mechanisms of polar, nonpolar and quadrupole molecules in CaA-type zeolites have not been thoroughly studied. In addition, there is not enough information about scientific research studies in which adsorption characteristics were studied by X-ray and spectroscopy methods, and adsorption enthalpy was studied.

## II. SIGNIFICANCE OF THE SYSTEM

Zeolites are currently the most important catalysts for the processing of various hydrocarbon raw materials. Synthetic CaA zeolites with different ratios of cations are highly effective catalysts for these processes. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

## III. METHODOLOGY

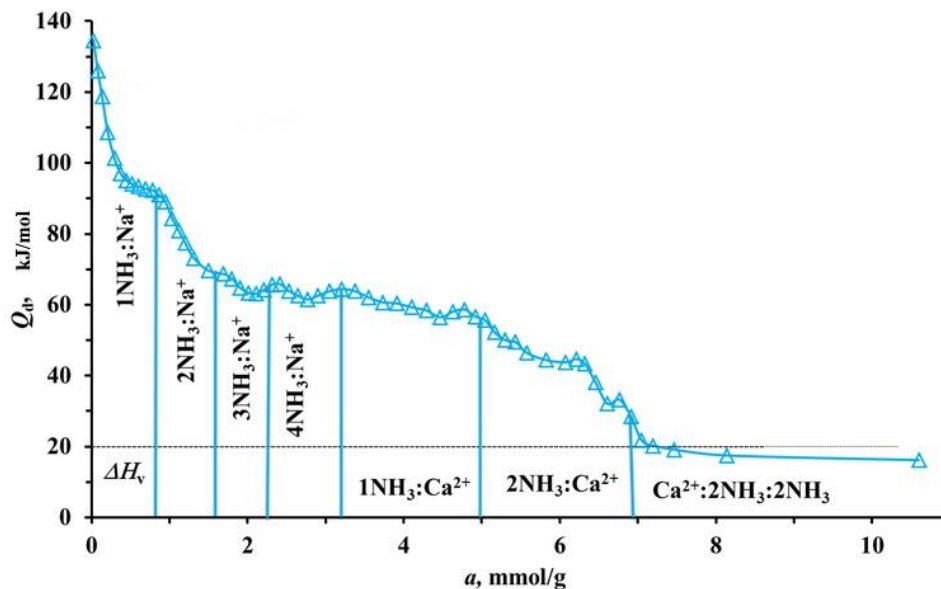
For measurements of isotherms and differential adsorption heats, a system consisting of a universal high-vacuum adsorption unit and a Tian-Calvet-type, DAC-1-1A thermally conductive differential microcalorimeter connected to it was used, which has high accuracy and stability. The instrument's calorimeter sensitivity is extremely high, and its reliability is high. It can be used confidently to measure the heat of processes of almost unlimited duration. The calorimeter makes it possible to obtain the thermokinetics of the process of adsorption systems under study, which is very important for elucidating the adsorption mechanism. Most of the heat (about 99%) released into the calorimeter chamber is dissipated into the calorimeter block immediately after release. Only about 1% of the heat released remains in the calorimeter chamber, raising its temperature slightly. The measurement is mainly concerned with the heat flux that passes through the surface of the calorimeter chamber and the calorimeter block. The adsorption-calorimetric method used in this work provides highly accurate molar thermodynamic characteristics and reveals detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. Adsorption measurements and adsorbate dosing were carried out using a universal high-vacuum adsorption unit. The unit allows adsorbate dosing by both gas-volume and volume-liquid methods. We used a BARATRON B 627 membrane pressure gauge to measure the equilibrium pressures.

## IV. EXPERIMENTAL RESULTS

In this article, the adsorption enthalpy and adsorption mechanism obtained by the method of adsorption-calorimetric experiment on synthetic zeolite of ammonia CaA (M-22) were presented. In the adsorption study, the adsorption mechanism was fully analyzed based on the differential enthalpy of ammonia adsorption on CaA (M-22) zeolite at 303 K. The unit cell composition of this zeolite is represented by  $\text{Ca}_{2,975}\text{Na}_{1,194}(\text{SiO}_2)_{12}(\text{AlO}_2)_{12}$  and consists of  $S_I$ ,  $S_{II}$  and  $S_{III}$  positions. Based on its chemical composition, the amount of calcium cations in 1 g of zeolite is 1,89 mmol/g and the amount of sodium cations is 0,76 mmol/g.

Figure 1 shows the differential enthalpy plot of ammonia adsorption on CaA (M-22) zeolite. In MFI, MOR, FAU, LTA and other zeolites, the differential heat (enthalpy) of adsorption of adsorbates of different nature changes stepwise [6-24]. The differential heat (enthalpy) of adsorption in the primary region is equal to 135 kJ/mol. As the amount of adsorption increases, the enthalpy at 0,37 mmol/g decreases linearly to 97 mol/g. The differential enthalpy of 0,76 mmol/g produces a step at adsorption. This value is equal to the number of sodium cations in the zeolite. A value of 0,37 mmol/g is half of the amount of sodium cations in zeolite. This is the result of each ammonia molecule interacting with 2 sodium

cations. Therefore, ammonia molecules are initially adsorbed on the sodium cations contained in the zeolite. Therefore, the formation of an enthalpy step at the adsorption amount of 0,76 mmol/g corresponds to the number of sodium cations in the zeolite, that is, the adsorbate/adsorbent monomer forms an ion-molecular complex  $1\text{NH}_3:\text{Na}^+$ .



**Figure 1. Differential heat of adsorption ( $Q_d$ ) of ammonia on zeolite CaA (M-22) at 303 K. The dashed line is the heat of condensation of ammonia at 303 K at 303 K.**

As the zeolite becomes saturated, the enthalpy decreases to 70 kJ/mol at an adsorption amount of 1,5 mmol/g, that is, ammonia molecules form a dimer  $2\text{NH}_3:\text{Na}^+$  ion-molecular complex with sodium cations. The differential enthalpy of formation of  $3\text{NH}_3:\text{Na}^+$  decreases from 70 kJ/mol to 63 kJ/mol initially, then increases to 65,7 kJ/mol at 2,3 mmol/g. A partial increase in enthalpy (by 2,7 kJ/mol) when all sodium cations of ammonia form a trimeric  $3\text{NH}_3:\text{Na}^+$  complex is the result of the release of additional energy as a result of the weak Van der Waals interaction of ammonia molecules.

The enthalpy first partially decreases, then increases again to 64 kJ/mol, forming a tetrameric  $4\text{NH}_3:\text{Na}^+$  complex at an adsorption amount of 3 mmol/g. From Fig. 1, it is clear that the stepwise change of the differential enthalpy is proportional to the amount of sodium cations (0,76 mmol/g). But the differential enthalpy of adsorption of the next ammonia molecule changes independently of the amount of sodium cations. Therefore, the adsorption process on sodium cations ends when ammonia molecules form a tetra  $4\text{NH}_3:\text{Na}^+$  complex in the first coordination sphere of zeolite with an adsorption amount of 3 mmol/g.

In the subsequent adsorption of ammonia molecules, the differential enthalpy decreases to 56,5 kJ/mol at the adsorption amount of 4,47 mmol/g and increases to 58 kJ/mol at the adsorption amount of 4,9 mmol/g. The difference between the amount of adsorption in the formation of the tetramer complex is equal to 1,9 mmol/g. This value is equal to the amount of calcium cations in the zeolite. So, ammonia molecules are adsorbed on calcium cations, and at 4,9 mmol/g adsorption, ammonia molecules form a  $1\text{NH}_3:\text{Ca}^{2+}$  monomer ion-molecular complex with calcium cations. Logically, in accordance with the amount of 1,9 mmol/g of calcium, the next change in the energy characteristics should be a sharp change in the differential enthalpy at the amount of 6,8-7 mmol/g of adsorption. This change can be sudden changes such as enthalpy increase from this value due to the formation of dimer-, tetramer complexes, decrease or create a step. From Fig. 1, it is clear that at 7 mmol/g adsorption amount, the differential enthalpy decreases from 58 kJ/mol, and the heat of condensation of ammonia decreases to 20 kJ/mol, forming the dimer complex  $2\text{NH}_3:\text{Ca}^{2+}$ . A decrease in the heat of condensation of ammonia to 20 kJ/mol represents the end of the adsorption process on calcium cations.

Further ammonia molecules are sorbed in the second coordination sphere, i.e. adsorbate/adsorbate. The differential enthalpy remains almost unchanged and the sorption process ends at the amount of adsorption of 10,6 mmol/g at a value equal to the heat of condensation of ammonia. The difference between this value and the amount of adsorption in the formation of the  $2\text{NH}_3:\text{Ca}^{2+}$  dimer complex is that the amount of calcium cations in the zeolite is twice as large as 1,9 mmol/g and is equal to 3,8 mmol/g. So, 2 ammonia molecules in the  $2\text{NH}_3:\text{Ca}^{2+}$  complex interact with the next 2 ammonia molecules to form the general complex  $\text{Ca}^{2+}:2\text{NH}_3:2\text{NH}_3$

**V. CONCLUSION AND FUTURE WORK**

In the adsorption-calorimetric study, the main thermodynamic characteristics of the adsorption of ammonia molecules on CaA (M-22) nanostructured zeolite were investigated. The differential enthalpy of adsorption was found to change stepwise depending on the amount of sodium and calcium cations in the zeolite. In the S<sub>I</sub> and S<sub>II</sub> positions of zeolite, sodium cations initially form tetramer 4NH<sub>3</sub>:Na<sup>+</sup> in the first coordination sphere, dimer 2NH<sub>3</sub>:Ca<sup>2+</sup> ion-molecular complexes with calcium cations in the first coordination sphere, then two ammonia molecules interact with the initially adsorbed ammonia molecules, that is, the adsorption process is formed in the second coordination sphere it was proved to be and form general Ca<sup>2+</sup>:2NH<sub>3</sub>:2NH<sub>3</sub> ion-molecular complexes.

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